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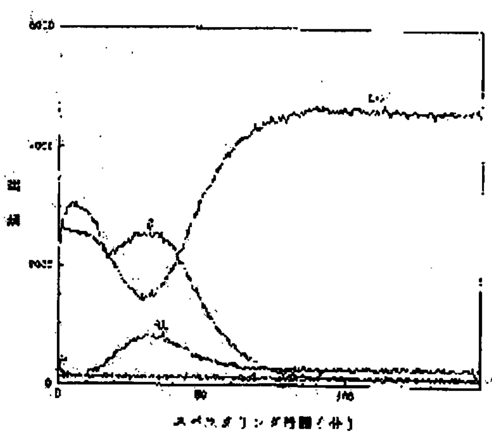
(54) SEMICONDUCTOR DEVICE AND FABRICATION THEREOF

(57)Abstract:
PURPOSE: To establish a technology allowing heat treatment required for enhancement of oxidation resistance at a specified temperature or below when a copper wiring material is used in a semiconductor device.
CONSTITUTION: In a semiconductor device having a thin film wiring of copper alloy containing 0.02-20 atomic % of aluminium and/or 0.02-20 atomic % of silicon, surface oxide is formed on the thin film wiring by heat treatment at 500°C or below. Al or Si is diffused from bulk part and concentrated in the oxide which thereby functions as a barrier layer against oxidation. The wiring bulk part resembles pure copper because Al or Si is diffused to the surface thereof thus exhibiting low resistance, EM resistance, and SM resistance inherent to copper. The copper alloy wiring thus formed has resistivity of 10μΩ.cm or below and oxidation resistance thus dealing with high integration of future semiconductor device.



LEGAL STATUS

Notes:
1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

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Dictionary: Last updated 12/14/2007 / Priority: 1. Electronic engineering / 2. Chemistry / 3. JIS (Japan Industrial Standards) term

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FULL CONTENTS

[Claim(s)]
[Claim 1] The semiconductor device characterized by having contained 0.02 - 20 atom % aluminum and/or 0.02 - 20 atom % silicon, and equipping the remainder with the thin film wiring which consists of a copper alloy which are copper and an inevitable impurity on a substrate.
[Claim 2] The semiconductor device according to claim 1 characterized by equipping the surface with the oxide film layer of this copper alloy.
[Claim 3] Claim 1 characterized by having aluminum and/or the preferential selective oxidation layer of silicon, or a semiconductor device according to claim 2.
[Claim 4] Claim 1 characterized by the resistivity of copper alloy wiring being below 10micro ohm-cm, or a semiconductor device according to claim 3.
[Claim 5] Contain 0.02 - 20 atom % aluminum and/or 0.02 - 20 atom % silicon, form on a substrate the thin film wiring which consists of a copper alloy whose remainders are copper and an inevitable impurity, and this thin film wiring is heat-treated at the temperature of 500 degrees C or less. The manufacture method of the semiconductor device characterized by forming an oxide film.

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the semiconductor device equipped with the copper alloy semiconductor thin film wiring containing a little aluminum and/or silicon on a substrate, and its manufacture method. Since the semiconductor device according to this invention is equipped with the copper wiring which resistivity is below 10micro ohm-cm, and is moreover excellent in oxidation

resistance, it can respond to increase of the degree of location in future Integrated Circuit Sub-Division etc.

[0002]

[Description of the Prior Art] Although aluminum containing Si etc. is conventionally used as wiring in the integrated circuit of a semiconductor device etc., if an element and the miniaturization of wiring progress with increase of a degree of location, increase and electromigration (EM) of a wiring resistance value will pose a problem. On the other hand, it originates in the difference of the thermal expansion of a wiring material and a base sheet with high integration, and what is called the problem of stress migration (SM) is also generated.

[0003] Rather than aluminum, by lower resistance, copper is considered that EM-proof nature and SM-proof nature are excellent, and is expected as a next-generation wiring material. However, copper is Si and SiO2 again that it is very easy to oxidize. There is a problem of being easy to react with a film etc., and this had become the inhibition factor of copper-wiring utilization.

[0004] As a policy of the oxidation-resistant improvement in this copper wiring, a barrier layer is formed on the surface of a copper wiring, diffusion of oxygen is prevented, and copper itself is Si and SiO2. Some trials it is made not to diffuse in a film are made. As one of the methods of forming, such a barrier layer [the collection of the 49th time of Showa 63(1988) autumn Japan Society of Applied Physics academic lecture meeting lecture drafts, 434 pages of the 2nd separate volume (1988), and 5 p-T-4] By heat-treating Cu-Ti film which carried out weld slag using the mosaic target which has arranged Ti on Cu at the temperature of 800 degrees C among nitrogen gas, a titanium nitride layer is formed and the method of excelling in oxidation resistance and moreover manufacturing the small copper wiring of resistivity is indicated.

[0005]

[Problem to be solved by the invention] However, a titanium nitride film is not necessarily thermodynamically stable at oxygen environment. and in order to form the copper wiring which equipped the surface with such a titanium nitride layer by self align (self aryne) You have to include 800-degree C heat treatment in the manufacture process of a semiconductor device. A heat-resistant temperature of the p-n junction usually formed in :(1) semiconductor device which needs to solve the following problems for that purpose is about 750 degrees C, and the heat treatment temperature of 800 degrees C is too high, (2) Consider it as the form which can use preferably the process currently used in the aluminum wiring semiconductor device from the former, and material as it is as much as possible (for example, organic materials, such as polyimide, cannot be used in the heat treatment temperature of 800 degrees C), (3) Don't receive big restrictions in the selection about the various material newly used with increase of a degree of location.

[0006] If not premised on self align (SERUFA line), it is also possible to form barrier layers, such as a titanium nitride layer, at low temperature comparatively, but the increase in a process number is not avoided in this case. The technical problem of this invention is establishing the technology the heat treatment temperature for facing in a semiconductor device using a copper wiring material, and raising oxidation resistance ending below 500 degrees C.

[0011] for example, the thing which is done for sputtering of the copper alloy target of the above-mentioned composition range in the case of the sputtering method -- or thin film wiring can be formed by the method of carrying out the weld slag of aluminum or a silicon target, and the copper target simultaneously. In the case of vacuum deposition, thin film wiring can be formed by [which heat the copper alloy evaporation source of the above-mentioned composition range] depending especially and making suitable copper for a case, aluminum, and/or the silicon compound of CVD react by a vapor phase state.

[0012] The Reason for making the average aluminum in the thin-film-wiring material in a semiconductor device and Si content into 0.02 - 20 atom % is that it will exceed the desirable range (limit) ohm-cm of 10micro of resistivity if the oxidation-resistant improvement effect will not be seen if less than 0.02 atom %, but it exceeds another side 20 atom %. If the resistivity of copper alloy wiring exceeds 10micro ohm-cm, use will not be borne as wiring of the semiconductor device of high integration.

[0013] In order to lower the residual strain and to lower resistivity, as for the formed thin film wiring, it is desirable to carry out annealing treatment at the temperature of 300-500 degrees C in a vacuum or an inert atmosphere. Only by this annealing treatment, by the remaining oxygen which exists slightly in atmosphere depending on composition of a wiring material, thin film wiring may oxidize and self-formation of the necessary oxide film layer may be carried out. When it contains especially aluminum, the oxidization effect required only of annealing treatment is acquired.

[0014] When oxidization operation sufficient by just the above-mentioned annealing treatment is not obtained, oxidization heat treatment for oxidizing thin film wiring is performed. It is one of the important points of this invention that this heat treatment temperature ends below 500 degrees C. If it exceeds 500 degrees C, a bad influence will begin to appear to the heat-resisting property of p-n junction [itself / of a semiconductor device]. And it originates in the difference of the thermal expansion of a wiring material and a base sheet, and exfoliation of a wiring part arises or a residual strain causes stress migration (SM) owing to. [that deterioration of the organic materials (for example, polyimide etc.) of a low dielectric constant used before and after wiring material formation takes place] if a small amount of remaining oxygen exists as a heat treating atmosphere -- a vacuum or an inert gas atmosphere -- any are sufficient and it may be among the atmosphere. Oxygen (:temperature:200-500 degree C and atmosphere:10-3-10Pa) or 1-atmosphere nitrogen-1-200 ppm oxygen, processing time which can carry out oxidation treatment on condition of following : 10 minutes - 2 hours [0015] In this way, an oxide film can be formed, carrying out diffusion concentration of aluminum or the Si near the wiring surface. Since aluminum and Si diffused the bulk section of wiring on the surface, it will be in the state near pure copper, and the lower resistance (below 10micro ohm-cm) which copper originally has, EM-proof nature, and SM-proof nature can be held. Therefore, the semiconductor device equipped with this wiring can respond to the increase in the degree of location of a future integrated circuit enough.

[0016]

[Working example] A work example and a comparative example are shown to below. In all these examples, the thin film wiring in a semiconductor device was formed by sputtering in the conditions of the next table 1.

[0007]

[Means for solving problem] In order to solve the above-mentioned technical problem, when examination was variously repeated paying attention to aluminum and silicone which are considered to form a stable and precise oxide film thermodynamically, the following knowledge is acquired and it came to accomplish this invention.

(1) The oxide film which carried out diffusion concentration of aluminum or the Si near the wiring surface can be formed by forming the copper alloy thin film wiring which does 0.02-20 atom % content of 0.02 to 20 atom %, and/or silicon for aluminum, and oxidizing this. This oxide film is excellent in oxidation resistance, and simultaneously, since aluminum and Si diffused the bulk section of wiring in the scaling film, it will be in the state near pure copper, and the lower resistance which copper originally has, EM-proof nature, and SM-proof nature can be maintained. Resistivity is below 10micro ohm-cm, and the formed copper alloy wiring has the outstanding characteristics corresponding to increase of the degree of location of moreover having oxidation resistance.

(2) The oxidation treatment of thin film wiring can hang down even the temperature of 500 degrees C or less.

[0008] Based on this knowledge, this invention contains (1) 0.02 - 20 atom % aluminum and/or 0.02 - 20 atom % silicon. It is what offers the semiconductor device characterized by having on a substrate the thin film wiring which consists of a copper alloy whose remainders are copper and an inevitable impurity. In this case, it is characterized by thin film wiring equipping the surface with the oxide film layer of this copper alloy especially aluminum, and/or the preferential selective oxidation layer of silicon, and is characterized by the resistivity of copper alloy wiring being below 10micro ohm-cm. This invention contains 0.02 - 20 atom % aluminum and/or 0.02 - 20 atom % silicon again. The thin film wiring which consists of a copper alloy whose remainders are copper and an inevitable impurity is formed on a substrate, this thin film wiring is heat-treated at the temperature of 500 degrees C or less, and the manufacture method of the semiconductor device characterized by forming an oxide film is offered.

[0009]

[Function] The copper alloy thin film wiring containing 0.02 - 20 atom % aluminum and/or 0.02 - 20 atom % silicon which were formed on the substrate of a semiconductor device forms a scaling film easily at the temperature of 500 degrees C or less. aluminum and Si from a wiring bulk section are carrying out diffusion concentration, and it is the stable precise oxide film, and this oxide film is excellent in oxidation resistance, and functions as a barrier layer. Simultaneously, since aluminum and Si diffused the bulk section of wiring in the scaling film, it will be in the state near pure copper, and the lower resistance which copper originally has, EM-proof nature, and SM-proof nature can fully be maintained. Since resistivity is below 10micro ohm-cm and the formed copper alloy wiring is moreover equipped with oxidation resistance, the semiconductor device equipped with this thin film wiring can respond to increase of the degree of location of a future semiconductor device.

[0010] 0.02 - 20 atom % aluminum and/or the copper alloy thin film wiring which carries out 0.02-20 atom % silicon content are formed on a substrate using the sputtering method, vacuum deposition, or the CVD and other gaseous phase forming-membranes method.

[0017]
[Table 1]

スパッタ条件	
ターゲット	3インチ（平板型）
投入電力	90W
Ar圧力	1Pa
基板温度	室温
膜厚さ	0．7μm
基板	SiO_2 被覆ガラス

[0018] The oxidation-resistant test in an example is a heat treatment test under the conditions of the following table 2.
[0019]
[Table 2]

耐酸化性テスト条件	
熱処理雰囲気	N_2-O_2 （1.4 ppm）混合ガス、1気圧
熱処理温度	450℃
熱処理時間	60分

[0020] (Work example 1-1: Semiconductor device equipped with the wiring containing comparatively much aluminum) The copper-alloy-wiring layer of aluminum content 12.3 atom % was formed in the substrate. First, the value was highly insufficient, although resistivity became 20.9micro ohm-cm and large aggravation was not seen, when the oxidation-resistant test was done about the film [having formed membranes] (resistivity: 17.9micro ohm-cm).
[0021] Next, when the film [having formed membranes] was heat-treated at 400 degrees C among the vacuum of 4x10 to 4 Pa for 1 hour (vacuum annealing treatment), resistivity was reduced to 9.8micro ohm-cm.
[0022] When this vacuum annealing film was further heat-treated at 450 degrees C among the atmosphere for 1 hour (oxidation treatment), resistivity did not have 9.9micro ohm-cm and change. The diffusion to the surface coat of aluminum and formation of an alloy oxide layer are accepted by the result as which drawing 1 analyzed in the depth direction from the surface of the "vacuum annealing + oxidization" processing film with Auger electron spectroscopy (AES). Before and after oxidation treatment, since there is no resistivity change, it is thought that it is in the state of drawing 1 only by vacuum annealing treatment.
[0023] a vacuum annealing film and a "vacuum annealing + oxidization" processing film -- it became

clear that all had oxidation resistance under a very severe condition.

[0024] (Work example 1-2: Semiconductor device equipped with the wiring containing a little aluminum) The copper-alloy-wiring layer of aluminum content 0.24 atom % was formed in the substrate. Next, it is a film [having formed membranes] (3.2micro of resistivity ohm-cm) N2 of latm The inside of a gas atmosphere, and (a) 300 degree C and (b) When heat-treated at 450 degree C for 1 hour (N2 annealing treatment in gas), resistivity is (a), respectively. 2.8 and (b) It became 2.8micro ohm-cm.

[0025] This N2 Annealing film in gas (a) When the oxidation-resistant test estimated, resistivity improved rather with 2.6micro ohm-cm, and it became clear that it had oxidation resistance.

[0026] (Work example 2-1: Semiconductor device equipped with the wiring containing comparatively many Si(s)) The copper-alloy-wiring layer of Si content 13.5 atom % was formed in the substrate. First, the value was highly insufficient, although resistivity became 16.2micro ohm-cm and a certain amount of reduction was seen, when the oxidation-resistant test was done about the film [having formed membranes] (resistivity: 45.9micro ohm-cm).

[0027] Next, when the same vacuum annealing treatment as a work example 1-1 was performed, what was 45.9micro of resistivity ohm-cm became 45.2micro ohm-cm immediately after membrane formation, and the reduction effect of resistivity was not seen. When the still more nearly same oxidation treatment (it is 1 hour at 450 degrees C among the atmosphere) as a work example 1-1 about a vacuum annealing film was added, resistivity became 6.1micro ohm-cm and it became clear that it had oxidation resistance under a very severe condition. The diffusion to the surface coat of Si and formation of an alloy oxide layer are accepted by the result as which drawing 2 analyzed the [vacuum annealing + oxidization] processing film in the depth direction from the surface by AES. Since resistivity decreased after oxidation treatment, in the stage of only vacuum annealing treatment, it is considered what has the diffusion to the surface coat of Si and formation of an alloy oxide layer more inadequate than the state of drawing 2 .

[0028] (Work example 2-2: Semiconductor device equipped with the wiring containing a little Si(s)) The copper-alloy-wiring layer of Si content 1.0 atom % was formed in the substrate. Next, it is a film [having formed membranes] (9.8micro of resistivity ohm-cm) N2 of latm The inside of a gas atmosphere, and (a) 300 degree C and (b) When heat-treated at 450 degree C for 1 hour (N2 annealing treatment in gas), resistivity is (a), respectively. 4.4 and (b) It became 4.5micro ohm-cm. Drawing 3 is 450 degrees C and N2 by AES. By the result of having analyzed in the depth direction from the annealing treatment membrane surface in gas, the diffusion to the surface coat of Si and formation of an alloy oxide layer are accepted. This N2 Annealing film in gas (a) When the oxidation-resistant test estimated, resistivity improved rather with 2.5micro ohm-cm, and it became clear that it had oxidation resistance.

[0029] (Semiconductor device equipped with the wiring containing work-example 3:aluminum and Si) In aluminum content, 2.1 atom % and Si content formed the copper-alloy-wiring layer of 2.2 atom % in the substrate. Next, it is a film [having formed membranes] (15.4micro of resistivity ohm-cm) N2 of latm It is (a) among a gas atmosphere. 300 degree C and (b) When heat-treated at 450 degree C for 1 hour (N2 annealing treatment in gas), resistivity is (a), respectively. 13.9 and (b) It became 12.5micro ohm-cm.

[0030] This N2 Annealing film in gas (a) When the oxidation-resistant test estimated, resistivity improved rather with 8.7micro ohm-cm, and it became clear that it had oxidation resistance.

[0031] (Comparative example 1: Semiconductor device equipped with pure copper wiring) The pure copper wiring layer was formed in the substrate. In order to evaluate the oxidation resistance of this copper wiring layer, when the oxidation-resistant test estimated, the sputter film oxidized and exfoliated from the substrate.
[0032] Next, (a) The same vacuum annealing treatment as a work example 1-1, and (b) Vacuum annealing treatment in 700 degree C, (c) It is N2 of 1 hour at 300 degree C. The annealing treatment in gas, and (d) It is N2 of 1 hour at 450 degree C. The place which performed annealing treatment in gas, That whose resistivity was 2.9micro ohm-cm in the state [having carried out weld slag] is (a), respectively. 2.3 and (b) 2.1 and (c) 2.0 and (d) It became 2.1micro ohm-cm.
[0033] This vacuum annealing film and N2 The place which was going to evaluate the annealing treatment film in gas by the oxidation-resistant test, Like the case of a film [having formed membranes], a sputter film oxidizes, exfoliates from a substrate and is vacuum annealing treatment or N2. Even if it processed the annealing treatment in gas, it became clear that a problem remained in a heat-resisting property.
[0034] (Semiconductor device equipped with comparative example 2-1:Cu-Ti alloy wiring) The copper-alloy-wiring layer of Ti content 15.0 atom % was formed in the substrate. When the oxidation-resistant test estimated the film [having formed membranes] (resistivity: 148micro ohm-cm), resistivity became 444micro ohm-cm, resistivity got worse sharply, and it became clear in the state [having formed membranes] that it did not have oxidation resistance.
[0035] In order to give oxidation resistance, when the vacuum annealing treatment same about a film [having formed membranes first] as a work example 1-1 was performed, resistivity became 52.3micro ohm-cm. When the oxidation-resistant test estimated this vacuum annealing film, resistivity became 49.9micro ohm-cm, and aggravation before and after a test was not seen, but temporary oxidation resistance was shown, but resistivity was highly inadequate.
[0036] Next, it heat-treated at 400 degrees C among 100Pa N2+H2 mixed-gas (50%) atmosphere for 1 hour in order to nitride a film [having formed membranes] (148micro of resistivity ohm-cm), and the resistivity of the wiring material became 48.8micro ohm-cm by this processing. When the oxidation-resistant test estimated this nitriding treatment film, resistivity improved rather with 18.4micro ohm-cm. Therefore, the nitriding film formed of nitriding treatment was unstable, and character's changing with subsequent oxidation treatments and the further oxidation treatment also proved that the improvement of resistivity is inadequate.
[0037] (Semiconductor device equipped with comparative example 2-2:Cu-Ti alloy wiring) The Cu-Ti alloy wiring layer was processed to the substrate on the same conditions as a comparative example 2-1 except the processing temperature by N2+H2 mixed gas (50%) having been 700 degrees C. It was the level which resistivity serves as 4.0micro ohm-cm, reduces more sharply than the case (48.8micro ohm-cm) of 400 degrees C, and can be used as a high accumulation wiring material by this processing. When the oxidation-resistant test estimated this nitriding treatment film, resistivity was not different from 4.0micro ohm-cm, the processing film formed of nitriding treatment was stable, and character did not change with subsequent oxidation treatments, but it was checked that it can be used as a high

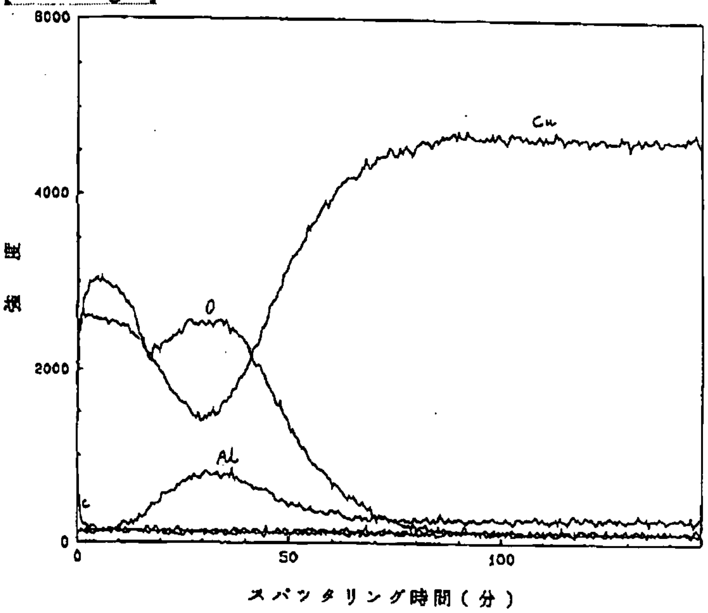
accumulation wiring material. Here, when vacuum annealing treatment of the film [having formed membranes] was carried out at 700 degrees C in order to eliminate the influence of atmosphere and to grasp the effect of only heat treatment, resistivity became 11.9micro ohm-cm (resistivity is 11.9micro ohm-cm also by an oxidation-resistant test), and the validity of nitriding treatment was checked.
[0038] Drawing 4 is the result of AES analyzing a nitriding treatment film in the depth direction from the surface. Since the peak of nitrogen lapped with Ti and was not able to distinguish, the analysis result by X-ray photoelectron spectroscopy (XPS) was attached as drawing 5 . It was imagined that, as for Ti near the surface, many form the oxide, and the part forms nitride from these results.
[0039] Thus, in the case of vacuum annealing treatment, desired resistivity was not obtained about the Cu-Ti alloy wiring layer, but the characteristics which can be used as a high accumulation wiring material by N2+H2 mixed-gas (50%) processing at 700 degrees C were able to be acquired. However, it is a problem as needing the temperature of 700 degrees C itself mentioned above.
[0040]
[Effect of the Invention] 1. Even if wiring miniaturizes in connection with high integration, the semiconductor device with which increase of a wiring resistance value is not seen is obtained.
2. The problem of electromigration (EM) is lost by that without increase of a wiring resistance value (that is, there is no increase of current density).
3. Since the difference of the thermal expansion of a wiring material and a base sheet is small, the problem of stress migration (SM) is lost.
4. It excels in the EM-proof nature of wiring, and SM-proof nature, and maintenance improvement of the reliability of a semiconductor device is carried out.
5. Excel in oxidation resistance and it is Si and SiO2. The copper-wiring barrier layer in which a film etc. and the formation by low-temperature self align which does not react are possible is realized, and the performance of a semiconductor device is improved.
6. The process and material which were used in the aluminum wiring semiconductor can use it almost as it is, and can suppress low the increase in the semiconductor device manufacture cost resulting from change of a wiring material, and an initial cost (construction cost) can also be made very low.

[Brief Description of the Drawings]
[Drawing 1] The result of having analyzed in the depth direction from the surface of the "vacuum annealing + oxidization" processing film with Auger electron spectroscopy (AES) in relation to the work example 1-1 is shown.
[Drawing 2] The result of having analyzed the vacuum annealing + oxidation treatment film in the depth direction from the surface by AES in relation to the work example 1-2 is shown.
[Drawing 3] It is connected with a work example 2-2, and is 450 degrees C and N2 by AES. The result of having analyzed in the depth direction from the annealing treatment membrane surface in gas is shown.
[Drawing 4] The result of having analyzed the nitriding treatment film in the depth direction from the

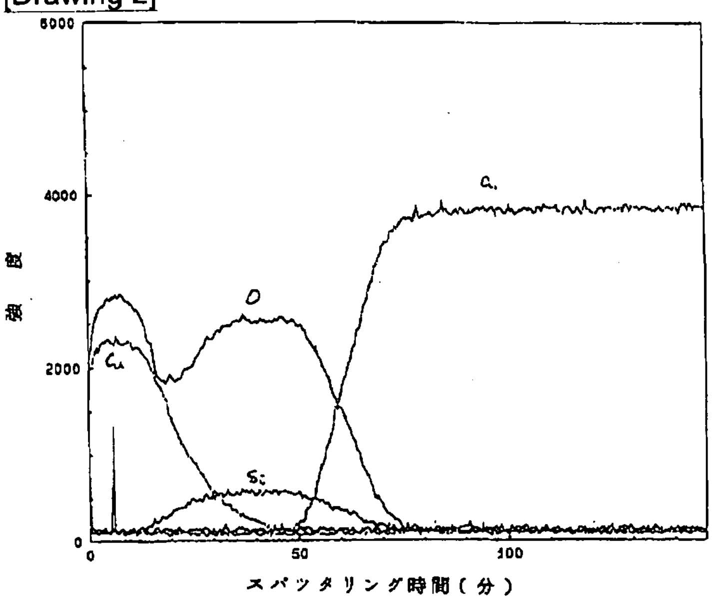
surface by AES in relation to the comparative example 2-2 is shown.

[Drawing 5] In relation to a comparative example 2-2, the analysis result by X-ray photoelectron spectroscopy (XPS) is shown.

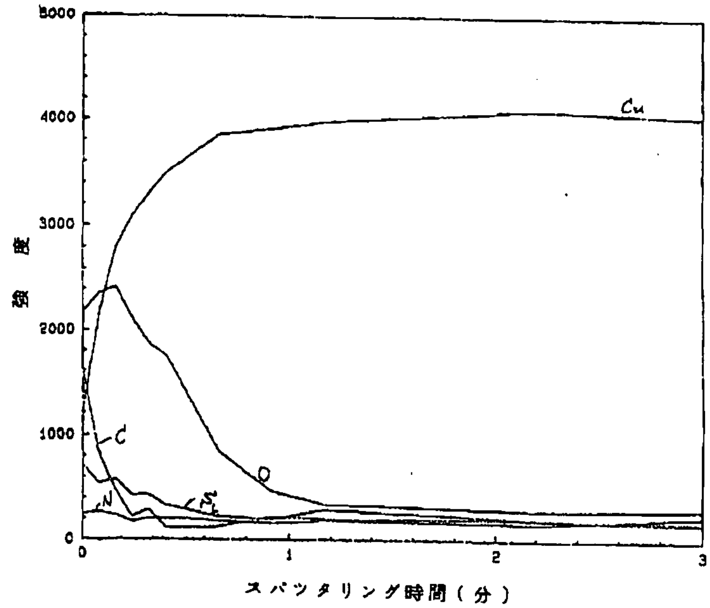
[Drawing 1]



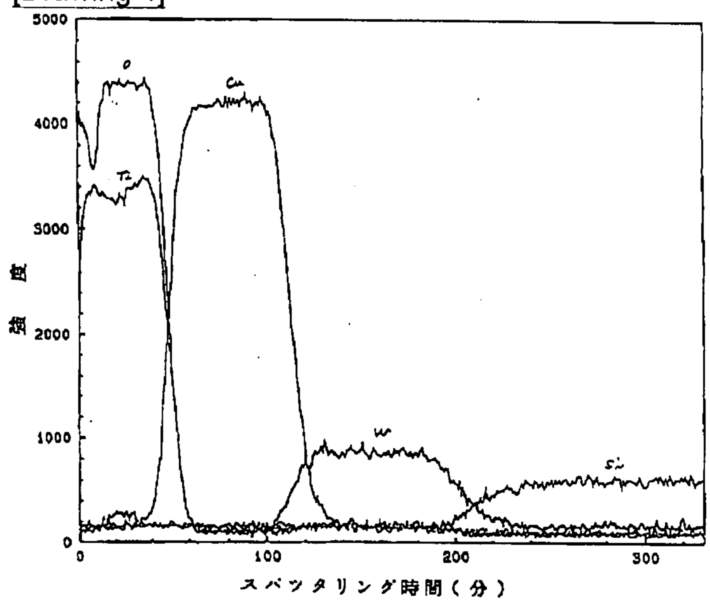
[Drawing 2]



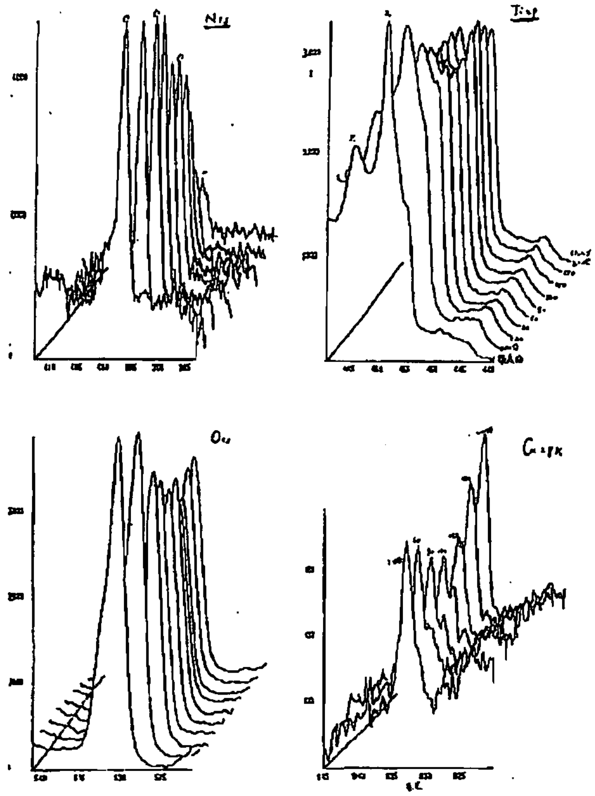
[Drawing 3]



[Drawing 4]



[Drawing 5]



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